8.—A NEW METHOD FOR THE DETERMINATION OF FERROUS IRON IN REFRACTORY SILICATES.

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INTRODUCTION.

The methods for the determination of ferrous iron in silicates have always presented difficulties to the mineral chemist and many investigators have carried out experiments with a view to improving them. The chief difficulties encountered are, the prevention of oxidation during the determination, and the incomplete decomposition of the more refractory silicates.

The determination of ferrous iron is an important question when deciding the constitution of the mineral, especially in the presence of both ferrous and ferric iron. The investigations described in this paper were carried out in an endeavour to evolve a method whereby the refractory silicates are completely decomposed without oxidation of the ferrous iron.

A survey of the methods in the literature at the disposal of the author shows that decomposition of the mineral is effected by either sulphuric acid or a mixture of hydrofluoric and sulphuric acids under varying conditions. In these investigations, the decomposition of the mineral was attempted by sintering or fusing in sealed glass tubes with a number of non-oxidising fluxes, with the final result that decomposition was effected by fusion with sodium metafluoborate.

Part I. of the paper describes the new method and its application to almandine garnet, the constitution of this mineral and the general application of the method to other minerals.

Part II. gives a brief description of the published methods, the necessity for the investigation, the complete investigations from which the new method was evolved and a consideration of the preparation, analysis and constitution of the fluoborates.

PART I.

The Method.

The determination of ferrous iron by this method depends on:—

1. The decomposition of the mineral by fusion with sodium metafluoborate in sealed pyrex glass tubes.

2. The solution of the fusion in dilute sulphuric acid solution in the absence of air.

3. The titration of the solution with standard potassium permanganate solution in the usual manner for the determination of iron.

Sodium metafluoborate $(NaF)_2.B_2O_3$.—The sodium metafluoborate is prepared by heating together 2 parts of anhydrous sodium fluoride and 1 part

of anhydrous boric acid in molecular proportions in a platinum dish at temperatures between 750° C. and 1050° C. At temperatures under 900° C. the heated pasty mass requires stirring with a platinum spatula. At temperatures over 900° C. a clear fusion is obtained in 5 minutes. Prolonged heating should be avoided above this temperature as fluorine is lost. The fused sodium metafluoborate is finely ground and kept in an air-tight bottle.

Glass Tubes.—The glass tubes are prepared from Pyrex glass tubing ½-inch in diameter, 1/32nd-inch thick and 2½ inches long. One end is sealed in the gas blast and the other end drawn out slightly to thin the glass, allowing sufficient opening to admit a short stemmed glass funnel for the introduction of the flux.

Procedure.—.3 to .5 grm. of the mineral, ground to pass 90-mesh sieve, is mixed with 5 times its weight of sodium metafluoborate on a glazed paper. The mixture is introduced into the glass tube by means of a short-stemmed glass funnel. Brush the paper and funnel, being careful to avoid the introduction of organic matter. The tube is gently tapped to pack the mixture, covered with .5 grm. of sodium metafluoborate, and quickly sealed. The sealed glass tube, containing the mixture of mineral and flux, is placed in a vertical position in a bath of sand and heated in an electric furnace at 950° C. for 15 minutes.

A convenient method of heating is as follows:—A Morgan Battersea "B" fireclay crucible is filled with glass sand (free from FeO). The glass tube is placed in the sand and completely covered. The fireclay crucible is covered with a flat fireclay or asbestos disc and placed in the furnace at the requisite temperature. Under these conditions the shape of the glass tube is perfectly retained and distortion through softening prevented.

The fireclay crucible is removed from the furnace and cooled sufficiently to permit the removal of the glass tube from the sand without distortion.

The hot glass tube containing the fusion is placed upon a fused silica square or in a platinum dish and covered to prevent loss of flying pieces on cooling. When cool, the glass is broken away from the fusion and the larger pieces of fusion broken to about the size of a pin's head.

The solution of the fusion is effected in the following manner:—Whilst the preceding operation is being carried out a solution of air free dilute sulphuric acid is prepared. Place 30 ccs. 10E H_2SO_4 and 150 ccs. distilled water in a 250 cc. flat-bottomed flask. Stopper the flask with a rubber cork through which a bent glass tube drawn to a fine nozzle at one end passes. Boil the solution and cool by placing the nozzle of the glass tube under a seal of sodium bicarbonate solution. When cool, the broken fusion and glass tube is added and the contents of the flask boiled on an asbestos mat over a bunsen burner. The neck of the flask should be held by a clamp, as bumping takes place. Ten minutes boiling should be sufficient for complete decomposition of the fusion. The flask is removed from the burner and allowed to cool under a sodium bicarbonate seal as before.

When cool, the stopper is removed and the solution titrated immediately with a standard $KMnO_4$ solution in the usual manner for the determination of iron.

A blank upon the reagents should be run under exactly similar conditions to the assay.

APPLICATION OF THE NEW METHOD TO ALMANDINE GARNET.

A sample of almandine garnet, Lab. No. 735/32, from the Yabberup District was prepared, analysed, and the ferrous iron determined by both the new fluoborate method and the hydrofluoric and sulphuric acid method as used in this laboratory.

Exp.	Garnet.	Fine.	$(NaF)_2$ B_2O_3	Ratio Flux to Mineral.	Temp.	Time.	FeO.	FeO.
							gms.	%
213	·4	—90	2·0	5 : 1	800°—850°C	20′	·1276	31·91
218	·4	,,	,,	,,	800°—900°C	,,	·1259	31·47
223	·5	Impalpable powder	2·5	,,	,,	,,	·1530	31·60
224	·4	—90	2·0	,,	900°—960°C	,,	·1262	31·56
225	·4	,,	2·0	,,	,,	,,	·1276	31·91

FeO by HF and H_2SO_4 method 30.30 per cent.
FeO mean figure by fluoborate method 31.69 per cent.

CONSTITUTION OF GARNET 735/32.

The mean figure 31.69 per cent. FeO was applied to the analysis of garnet 735/32 and the ratio of molecules RO : R_2O_3 : SiO_2 calculated and compared with the ratio obtained by using the FeO figure by the HF and H_2SO_4 method.

Theoretically almandine garnet has the following ratio:—
RO : R_2O_3 : SiO_2 :: 3 : 1 : 3.

Analysis.	FeO by HF. H_2SO_4 method.		FeO by fluoborate method.	
	%	Mols.	%	Mols.
SiO_2	35·29	5,876	35·29	5,876
Al_2O_3	19·25	1888	19·25	1,888
Fe_2O_3	3·31	207	1·77	111
FeO	30·30	4,218	31·69	4,411
MnO	1·47	207	1·47	207
CaO	3·50	624	3·50	624
MgO	3·36	833	3·36	833
H_2O+	·62	344	·62	344
H_2O- ...	—			
TiO_2	3·14	393	3·14	393
Total ...	100·24		100·09	

MICROSCOPIC EXAMINATION.

Small amount of black mineral—Ilmenite.
Smaller amount of red brown mineral—Limonite.
Smaller amount of colorless mineral—Quartz.
Traces of amphibole and altered minerals.

RATIO RO : R_2O_3 : SiO_2 IN GARNET 735/32.

R_2O_3 after deducting all Fe_2O_3 molecules calculated to limonite and RO after deducting 393 *mols. FeO to balance TiO_2 to ilmenite.*

	Ratio.				
	RO	:	R_2O_3	:	SiO_2
1. By HF and H_2SO_4 method	2·91	:	1	:	3·11
2. By Fluoborate method	3·01	:	1	:	3·11

All Fe_2O_3 mols. added to R_2O_3 and RO after deducting 393 mols. FeO to balance TiO_2 to ilmenite.

		Ratio.				
		RO	:	R_2O_3	:	SiO_2
3.	By HF and H_2SO_4 method	2·62	:	1	:	2·80
4.	By Fluoborate method	2·84	:	1	:	2·94

R_2O_3 after deducting all Fe_2O_3 mols. calculated to limonite and RO including all FeO mols. with TiO_2 left uncombined.

		Ratio				
		RO	:	R_2O_3	:	SiO_2
5.	By HF and H_2SO_4 method	3·12	:	1	:	3.11
6.	By Fluoborate method	3·22	:	1	:	3.11

All Fe_2O_3 mols. added to R_2O_3 and RO including all FeO mols. with TiO_2 left uncombined.

		Ratio				
		RO	:	R_2O_3	:	SiO_2
7.	By HF and H_2SO_4 method	2.81	:	1	:	2·80
8.	By Fluoborate method	3·04	:	1	:	2·94

Comments.

The ratio of 3.01 : 1 : 3.11 in No. 2 by using the FeO value obtained by the fluoborate method gives a closer agreement with the theoretical ratio of 3 : 1 : 3 than the ratio 2.91 : 1 : 3.11 obtained by using the FeO value obtained by HF and H_2SO_4 method. The recognition of ilmenite and limonite in the sample justifies the calculating of the Fe_2O_3 to limonite and the combining of 393 mols. of FeO to balance 393 mols. of TiO_2 to form ilmenite. The presence of quartz in the sample is shown by the higher ratio for SiO_2, 3.11.

When the Fe_2O_3 molecules are added to the R_2O_3 molecules as in 3, 4, 7 and 8, the ratio of 3 : 1 : 3 is upset, and when the TiO_2 molecules are not combined with FeO molecules as in 5, 6, 7 and 8, the ratio of SiO_2 is less than that of RO which cannot be owing to presence of free quartz in the sample.

The above calculations therefore prove that the figure obtained by the fluoborate method is the correct one.

Check FeO Determinations on Garnet 735/32.

New batches of sodium fluoborate were prepared and the method again applied to the almandine garnet sample, Lab. No. 735/32.

Exp.	Garnet 735/32.	Fine.	$(NaF)_2$ B_2O_3	Ratio Flux to Mineral.	Temp.	Time.	FeO.	FeO.
							gms.	%
244	·3	—90	1·5	5 : 1	900°—960°C	20′	·0956	31·87
289	·4	,,	2·0	,,	,,	15′	·1264	31·60
291	·45	,,	2·25	,,	,,	,,	·1417	31·49

The mean FeO figure by fluoborate method in this series is 31.65 per cent. and checks the mean figure of 31.69 per cent. in Experiments 213, 218, 223-5.

THE FLUOBORATE METHOD APPLIED TO OTHER MINERALS.

The determinations up to the present stage have been carried out upon almandine garnet and satisfactory results obtained which are confirmed when the FeO figure is applied to the constitution of this mineral.

To prove the general application of the method to silicate minerals, experiments were carried out on samples of biotite mica, staurolite, axinite and tourmaline. The first one tried, biotite, was chosen on account of the ease with which it is decomposed by HF and H_2SO_4, giving a figure which can be compared with the figure obtained by the fluoborate method. The next tried were staurolite, axinite and tourmaline. These are refractory minerals only being partly decomposed by HF and H_2SO_4 even when finely ground. For comparison with the fluoborate method a figure for FeO was obtained by treating the finely ground product with HF and H_2SO_4, weighing the undecomposed residue and calculating the FeO value upon the weight of decomposed mineral obtained by difference.

BIOTITE SAMPLE.

Analysis, 4064/32, *Holleton*.

	%
SiO_2	34·28
Al_2O_3	19·91
Fe_2O_3	7·25
*FeO	17·24
MnO	·28
MgO	5·53
CaO	·01
Na_2O	·38
K_2O	9·24
H_2O+	3·45
H_2O-	·52
TiO_2	1·67
P_2O_5	·23
Total	99·99

* By HF and H_2SO_4 method.

EXPERIMENT WITH 5 : 1 MIXTURE $(NaF)_2.B_2O_3$: BIOTITE.

Exp.	Biotite. 4064/32	$(NaF)_2$ B_2O_3	Temp.	Time.	FeO gms.	FeO %	Conditions.
317	·3	1·5	900—960°C.	15′	·0517	17·24	Good fusion. Complete decomposition.

The sodium fluoborate used in this experiment was batch 279 and had been standing in a stoppered bottle for six months after preparation. There was no sign of decomposition or attack upon the glass.

	HF and H_2SO_4 method.	Fluoborate method.
FeO ...	17·24%	17·24%

STAUROLITE SAMPLE.

Analysis, 733/32, Chittering Lake.

	%
SiO_2	30·08
Al_2O_3	49·94
Fe_2O_3	1·56
*FeO	12·98
MnO	·42
MgO	1·54
CaO	·38
Na_2O	·14
K_2O	·06
H_2O+	1·92
TiO_2	·90
Total	99·92

* By HF and H_2SO_4 method.

EXPERIMENTS WITH 5 : 1 MIXTURE $(NaF)_2.B_2O_3$: STAUROLITE.

Exp.	Staurolite 733/32 —90 mesh.	$(NaF)_2$ B_2O_3	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
302	·3	1·5	900—960°C.	15′	·0353	11·78	Good fusion. Complete decomposition.
309	·5	2·5	do.	15′	·0583	11·66	do. do.
314	Fine ·5	2·5	do.	15′	·0583	11·66	do. do.

The method and conditions observed were similar to those with garnet and biotite.

	HF and H_2SO_4 method.		Fluoborate method.
FeO	12·98%	...	11·70%

AXINITE SAMPLE.

Analysis, 2413/29, Talbot Bay.

	%
SiO_2	42·14
Al_2O_3	17·67
Fe_2O_3	1·74
*FeO	6·81
MnO	3·09
MgO	2·06
CaO	19·96
B_2O_3	5·56
H_2O+	1·56
Total	100·59

*By HF and H_2SO_4 method.

EXPERIMENTS WITH 5 : 1 MIXTURE $(NaF)_2.B_2O_3$: AXINITE.

Exp.	Axinite 2413/29.	$(NaF)_2$ B_2O_3	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
303	·3	1·5	900—960°C.	15′	·0180	6·00	Good fusion. Complete decomposition.
310	·5	2·5	do.	15′	·0281	5·62	do. do.
312	·5	2·5	do.	15′	·0305	6·11	do. do.
316	·5	2·5	do.	15′	·0288	5·76	do. do.

The method and conditions observed were similar to those with garnet, biotite and staurolite.

	HF and H_2SO_4 method.		Fluoborate method.
FeO	6·81%	...	5·87%

TOURMALINE SAMPLE.

*FeO 12·41%

*By HF and H_2SO_4 method.

EXPERIMENTS WITH 5 : 1 MIXTURE $(NaF)_2.B_2O_3$: TOURMALINE.

Exp.	Tourmaline —90 mesh.	$(NaF)_2$ B_2O_3	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
290	·4	2·0	900—960°C.	15′	·0492	12·30	Good fusion. Complete decomposition.
294	·3	1·5	do.	15′	·0371	12·36	do. do.

The method and conditions observed were similar to those with garnet, biotite, staurolite and axinite.

	HF and H_2SO_4 method.		Fluoborate method.
FeO	12·41%	...	12·33%

SUMMARY.

A new method for the determination of ferrous iron in refractory silicates is described. It consists of the fusion of the mineral with sodium metafluoborate $(NaF)_2.B_2O_3$ in sealed pyrex glass tubes, the solution of the fusion in dilute sulphuric acid solution and the titration of the solution with standard potassium permanganate solution.

Consistent ferrous iron figures are obtained upon a sample of almandine garnet with different batches of sodium metafluoborate.

The accuracy of the ferrous iron figures obtained is supported by—

1. The calculation of the constitution of the garnet.
2. The results obtained with biotite, a mineral completely and easily decomposed by a mixture of hydrofluoric and sulphuric acids.

The method is applicable to other minerals with satisfactory results. Minerals such as tourmaline, staurolite and axinite, which are not completely decomposed with hydrofluoric and sulphuric acids, are completely decomposed by fusion with sodium metafluoborate without further fine grinding of the −90 mesh product.

PART II.

Before proceeding with a description of the experimental work in connection with this method, a brief description of the existing methods will be outlined and the reasons necessitating an attempt to develop a new method presented.

HISTORY.

In all the known methods for determination of FeO in minerals, the decomposition is effected by either sulphuric acid alone or by a mixture of hydrofluoric and sulphuric acids.

METHODS EMPLOYING SULPHURIC ACID ALONE.

Mitscherlich's Method[2].—In this method the extremely fine ground mineral is heated in a sealed glass tube with a strong sulphuric acid solution (4 parts acid to 1 of H_2O) at a temperature of 200° C. The resulting solution is titrated with standard $KMnO_4$.

Mitscherlich's Method modified[2].—The modification uses a much weaker solution of sulphuric acid to allow for the solution of separated salts, the proportion of acid to water being 1 : 3. The air in the tube is replaced by CO_2 before sealing.

METHODS EMPLOYING SULPHURIC ACID AND HYDROFLUORIC ACID.

Suida's Method.[1]—The mineral is ground until it will remain in suspension in water at least two hours. This finely ground product is decomposed by a mixture of HF and H_2SO_4 in a sealed glass tube. The solution is titrated with standard $KMnO_4$ solution.

Pratt's Method modified.[3]—Pratt uses the coarsest powder that can successfully be decomposed. The mineral is placed in a platinum crucible of 80-100 cc. capacity with a little air free water and about 10 cc. of H_2SO_4 (1 acid to 3 water by volume). Air free hot water is added until the crucible is half full. The crucible is covered, placed upon a triangle and heated at low heat. The air is displaced by CO_2 introduced under the lid, 5-7 ccs. of strong HF added, the cover replaced and the solution boiled for 5-10 minutes. The crucible with contents is then transferred into a titrating vessel containing a cold saturated solution of boric acid in freshly boiled water, and titrated with standard $KMnO_4$ solution. Any undecomposed residue is finely ground and re-treated.

Cooke's Method.[4]—This method is similar to Pratt's modified method in that the mineral is decomposed by H_2SO_4 and HF in an atmosphere of CO_2. More elaborate apparatus (including a water trap) is, however, used to hold the atmosphere of CO_2 around the crucible to prevent oxidation by air. The time of treatment is increased in this method to one hour.

Barneby's Method.[5]—Barneby uses a simplified form of Cooke's apparatus. Steam is used instead of CO_2 to expel the air. The water trap is replaced by a phosphoric acid solution (1:2).

Treadwell's Method.[6]—The decomposition of the mineral in this method is effected in a similar manner to the former methods. The platinum dish containing the mineral is placed in a specially designed lead box and is heated in a paraffin bath at a temperature of 120° C. for about two hours in an atmosphere of CO_2.

W.A. Government Chemical Laboratory Method.—.5 grm. of mineral crushed to pass a 90 mesh sieve is placed in a special platinum crucible of 30 ccs. capacity. 15 ccs. 1OE H_2SO_4 and 5 ccs. HF are added to the crucible which is immediately covered. Place the crucible and contents upon a sand bath and boil for seven minutes. Remove and place in a 400 cc. beaker containing 200 ccs. of freshly boiled water in which 1 grm. of boric acid has been dissolved. Detach the lid with a glass rod, stir well and titrate with standard $KMnO_4$ solution.

The special platinum crucible is of 30 ccs. capacity and has a close fitting double lid, each piece of which has a small central aperture and is separated from the other by a plain platinum disc. A platinum wire holder is used for lifting the crucible.

In cases with refractory minerals where incomplete decomposition is obtained, the residue is either weighed and the FeO value obtained by calculation or it is reground and retreated with H_2SO_4 and HF.

COMMENTS.

Mitscherlich's method with H_2SO_4 alone has not proved satisfactory owing to the length of time required for the decomposition of the mineral which, in some cases, as with tourmaline, is never complete, the excessive fine grinding necessary which may cause oxidation,[1] and the difficulties in manipulation.

The methods using HF and H_2SO_4 increase the rate and amount of decomposition, but these acids do not give complete decomposition of refractory minerals, such as tourmaline, even when finely ground. It is necessary to either re-treat the residue after further grinding or weigh the residue and obtain the FeO value by calculation. The former is not altogether satisfactory on account of the possibility of errors introduced due to oxidation and manipulation. The latter may be used in the case of homogeneous minerals, but, generally speaking, it is unsatisfactory owing to doubt as to the composition of the residue.

The main line of investigation in respect to all these methods seems to have been confined to the prevention of oxidation of the FeO from a number of sources during decomposition of the mineral. There does not appear to have been any practicable method evolved in which complete decomposition of the more refractory minerals has been attained even with excessive fine grinding.

It was therefore decided to investigate the possibility of developing a method by fusing the mineral with suitable fluxes.

The Evolution of the Method.

As the decomposition of the mineral is to be effected by fusion with fluxes, the main problems presenting themselves are:—

1. The selection of the fluxes which will not cause oxidation of the ferrous iron.
2. The method to be adopted in carrying out the fusion without oxidation by oxygen from the air.

It was decided, with regard to the latter, to carry out the fusion in sealed combustion glass tubes. The flowing point of combustion glass is about 900° C., therefore the fluxes first considered were those whose melting

points are under this temperature. Later means were devised for heating the glass tubes at temperatures over 900° C., and fluxes of higher melting point were considered. The effect of sintering as well as fusing was also tried. Combustion glass was replaced by pyrex glass.

A study of suitable materials, and their melting points, for fluxes led to preliminary experiments being carried out with potassium hydroxide, sodium hydroxide, and the alkali fluorides. Of these sodium fluoride and potassium fluoride showed the most promise, and further investigations were carried out with these salts alone and in mixtures with potassium acid fluoride, calcium fluoride, and sodium hydroxide. Finally, mixtures of fluorine and boron compounds were tried and resulted in the preparation of sodium metafluoborate, a flux which will completely decompose silicate minerals with satisfactory ferrous iron results.

PRELIMINARY EXPERIMENTS.

A number of trial experiments were carried out upon garnet and tourmaline with KOH, NaOH, KF, NaF, and CaF_2, using glass tubes made from ordinary combustion tubing ½-inch in diameter, to ascertain the best conditions under which to carry out the investigations. The heating was carried out in the direct flame of the bunsen and meker burners and in an electric furnace at temperatures between 700° C. and 960° C. Softening and distortion of the glass tubes, causing complete collapse in some cases, rendered the experiments useless.

To prevent this collapse the glass tubes were placed in a bath of sand and heated in the electric furnace at the above temperatures. This proved satisfactory and was adopted in the subsequent experiments.

The ordinary glass combustion tubing was replaced by pyrex glass tubing, ½-inch diameter, on account of its greater resistance to heat, its ability to withstand change of heat without cracking, its resistance to chemical action and its low iron content.

Method of Procedure.

As a result of the conditions observed in the trial experiments, the following method of procedure was adopted in the subsequent investigations.

Mix the finely ground mineral with the desired amount of flux on a mixing paper and introduce in the glass tube by means of a short-stemmed glass funnel. The tubes are made from pyrex glass tubing ½-inch diameter, 1/32-inch thick and about 2½ inches in length. One end is sealed in the gas blast. The tube containing the mixture is gently tapped, covered with a layer of flux and the open end quickly sealed. Place the tube vertically in a bath of sand with about ¼ inch exposed. The sand bath consists of a Morgan Battersea "B" fireclay crucible filled with glass sand from Lake Gnangara, containing .03 per cent. Fe_2O_3 and no FeO. The size of the glass tube and sand bath is limited to the size of the Gallenkamp's electric furnace used.

The sand bath containing the sealed glass tube and contents is placed in the electric furnace at the desired temperature. At the expiration of the requisite time of heating it is removed and allowed to cool sufficiently so that the glass tube can be removed without distortion.

The hot tube is placed in a 250 cc. stoppered flask containing 30 cc. IOE H_2SO_4 made up to 200 cc. with distilled water in which 1 grm. of B_2O_3 has been dissolved, the whole solution having been boiled and cooled in an

atmosphere of CO_2 as in the usual manner for the determination of iron. The stopper consists of a rubber cork through which a bent glass tube drawn to a fine nozzle passes. The atmosphere of CO_2 is obtained by placing the nozzle of the flask containing the hot solution under a saturated solution of sodium bicarbonate.

Boric acid[12] is added to the solution to render the fluorine inactive by the formation of fluoboric acid (HBF_4) which does not appreciably dissociate to form HF. The plunging of the hot tube into the cold solution causes the glass to crack away and open up the sinter or fusion.

The stoppered flask containing the assay is placed upon an asbestos mat over a bunsen burner and boiled until solution is complete. It is then allowed to cool by placing the nozzle under sodium bicarbonate solution as before. When cool, the solution is titrated with standard $KMnO_4$ solution and FeO calculated in the usual manner.

EXPERIMENTS WITH KOH AND NaOH.

These substances were first tried on account of their low melting points, KOH being 360.4° C. and NaOH 318.4° C. Experiments were carried out by fusing tourmaline with them at temperatures of 600°-800° C. They, however, proved unsatisfactory owing to the rapidity with which they pick up water, rendering the mixing of the flux and mineral a difficult process. The presence of water in the mixture caused the mass to froth and the glass tubes to crack. No definite figures for FeO could be obtained.

EXPERIMENTS WITH ALKALI FLUORIDES.

The effect of fluorides was next tried as their action as a flux in ore magmas is well known.

Fluorides are stable salts to heat. J. Newton Friend (8) says, "Most fluorides are stable bodies not being decomposed by heating either alone or with carbon." Watt's Dictionary of Chemistry says, "Ferrous fluoride is unchanged by heat." J. Newton Friend (9) gives the volatilization temperature of ferrous fluoride as 1100° C. and ferric fluoride as 1000° C.

Melting points as given by various authorities:—

KF	...	789°C, 846°C, 859·9°C, and 867°C.
NaF	...	980°C, 986°C, and 988°C.
CaF_2	...	1360°C.

The effect of fusions with the lower M.P. fluorides and sinters with those of high M.Ps. was tried either alone or in mixtures by varying the temperature, time of heat treatment and the ratio of mineral to flux.

Potassium fluoride was first used on account of its low melting point. Experiments conducted by fusing both tourmaline and garnet at temperatures between 800°-900° C. proved unsatisfactory owing to the rapidity with which KF picks up water, and as in the case with the alkaline hydroxides no definite figures for FeO could be obtained.

Sodium fluoride was next tried. This substance does not pick up water as readily as the potassium salt and could be quite easily mixed with the

mineral. Experiments carried out by the foregoing method on samples of garnet and tourmaline gave the following results:—

Exp.	Garnet 459.	Flux NaF.	Temp.	Time.	FeO.	FeO.	FeO, HF H_2SO_4	Conditions.
					gms.	%	%	
23	·3	1·0	700—800°C	15′	·0318	10·6	19·1	Sinter.
24	·3 Tourmaline.	1·0	960—1000°C.	15′	·0512	17·1	...	Fusion.
28	·3	1·0	960—1040°C.	5′	·0273	9·1	14·5	Sinter.
29	·3	1·0	960—1040°C.	10′	·0307	10·2	...	Partial fusion.
30	·3	1·0	do.	10′	·0328	10·9	...	do.
31	·4	1·3	do.	10′	·0419	10·5	...	do.

Experiment 24 gave about 90 per cent. of the FeO obtained by the HF and H_2SO_4 method on garnet.

Experiment 30 gave about 75 per cent. of the FeO obtained by the HF and H_2SO_4 method on tourmaline.

Experiments 23 and 28 with sinters showed a small residue insoluble in sulphuric acid solution.

Experiments 24, 29-31 showed a small amount of fusion combined with the glass which was not completely soluble in sulphuric acid solution.

Generally speaking, the conditions and behaviour were much more satisfactory than those observed with the alkaline hydroxides and potassium fluoride. It was therefore decided to conduct more detailed investigations.

GARNET SAMPLE.

For subsequent experiments a sample of almandine garnet, Lab. No. 806, from Yabberup was prepared and analysed. This mineral was chosen on account of its refractoriness to hydrofluoric and sulphuric acids, although a figure for FeO can be obtained by the method used in this laboratory and described under the history of the methods. A microscopic examination of the residue after solution always revealed the presence of minute particles of undecomposed garnet, however finely the mineral was ground.

Analysis.

	%	
Al_2O_3	23·97	
Fe_2O_3	3·22	
*FeO	29·18	average of 4 results.
MnO	1·04	
CaO	3·44	
MgO	3·68	

* FeO determined by the H_2SO_4 and HF method on the finely ground garnet gave the following results:—

Exp. 32	29·94	FeO
„ 34	29·11	„
„ 37	29·04	„
„ 46	28·62	„

A microscopic examination of the residue revealed the presence of minute particles of undecomposed garnet.

EXPERIMENTS WITH 10 : 1 MIXTURE NaF : GARNET.

Sodium fluoride prepared in the laboratory from sodium carbonate (BDH., AR.) and hydrofluoric acid (Baker's anal., C.P.) was used in these experiments.

Exp.	Garnet 806.	NaF.	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
33	·3	3·0	960—1040°C.	10′	·0887	29·6	Fusion.
35	·4	4·0	do.	10′	·1132	28·3	Partial fusion. Combination with glass. Fusion not completely soluble.
36	·5	5·0	do.	10′	·1256	25·1	Fusion. Less soluble than 33 and 35.

The results indicate that, under certain conditions, garnet is decomposed without oxidation. In Exp. 33 the FeO content is only slightly lower than the highest result obtained in Exp. 32 by the HF and H_2SO_4 method.

Before proceeding with further experiments with sodium fluoride, the effect of mixtures of potassium acid fluoride and garnet in the ratio of 6 : 1 were tried.

Potassium acid fluoride when heated evolves HF and was tried to see if the HF generated would prevent oxidation by replacing the air in the tube.

EXPERIMENTS WITH 6 : 1 MIXTURE KHF_2 : GARNET.

Exp.	Garnet 806.	KHF_2	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
40	·5	3·0	960—1040°C.	15′	·0386	7·7	Partial fusion and combination with glass. Tube blown out.
41	·5	3·0	do.	20′	·0140	2·8	Complete fusion and combination with glass. Tube blown out.
42	·5	3·0	do.	25′	...	...	do. do.
43	·5	3·0	800°C.	20′	·0370	7·4	Sinter. Tube blown out.
44	·5	3·0	800—850°C.	60′	...	...	Complete fusion and combination with glass.

The HF liberated from the KHF_2 on heating caused the tubes to blow out. Higher temperatures with the lower M.P. of the potassium fluoride formed, caused excessive combination with the glass and incomplete solution of the fusion in sulphuric acid.

Experiments with NaF were continued by sintering at a temperature of 850°-960° C. (which is below the M.P. of NaF) with a 6 : 1 mixture of NaF : garnet, the NaF used being the pure reagent from F.G.B.

Experiments with 6 : 1 mixture of NaF pure : garnet.

Exp.	Garnet 806.	NaF F.G.B.	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
47	·5	3·0	850—960°C.	25′	·0690	13·8	Sinter. Compact
48	·5	3·0	do.	25′	·0955	19·1	do. do.
49	·5	3·0	do.	60′	·0840	16·8	Undecomposed mineral.
50	·5	3·0	do.	30′	·0960	19·2	do. do.

In this series the disintegration and solution of the sinter was slow and incomplete.

Experiments with 10 : 1 mixture of NaF pure : garnet.

These experiments were carried out to see if the increased amount of NaF caused the sinters to disintegrate more readily upon boiling at the temperature used in Exp. 47-50.

Exp.	Garnet 806.	NaF F.G.B.	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
52	·3	3·0	850—960°C.	30′	0·687	22·9	Black sinter. Not completely soluble.
53	·3	3·0	do.	60′	·0624	20·8	do. do.
54	·3	3·0	do.	30′	·0696	23·2	do. do.
55	·3	3·0	do.	20′	·0729	24·3	do. do.
56	·3	3·0	do.	15′	·0717	23·9	do. do.
57	·3	3·0	do.	10′	·0579	19·3	Not sintered properly. Undecomposed mineral.
58	·3	3·0	do.	10′	·0495	16·5	do. do.
59	·3	3·0	do.	15′	·0666	22·2	Black sinter not completely soluble.
63	·3	3·0	960—1040°C	10′	·0669	22·3	do. do.

The 10:1 mixtures sinter well and disintegrate more readily than the 6:1 mixtures but are still incompletely soluble.

The best conditions obtained were those by heating at 850-960° C. for 15 minutes, or 960-1040° C. for 10 minutes. The glass was not appreciably attacked.

The low results obtained are due to either—

(a) Incomplete decomposition of the garnet, or

(b) Oxidation of the FeO during experiment.

Experiment 71 was carried out to see if any oxidation took place in boiling a solution of NaF with H_2SO_4 and B_2O_3 solution.

Control Experiment.

Exp. 71.—.1018 grm. Standard Steel (99.64 per cent. Fe) was dissolved in 30 ccs. 10E H_2SO_4 and made up to 200 ccs. with freshly boiled water in a 250 cc. stoppered flask. 1.0 gms. NaF and 1.0 gms. B_2O_3 were

then added and the whole boiled for 15 minutes. This solution was cooled and treated as in the previous experiments. .1018 gms. Standard steel (99.64 per cent. Fe) added = .1014 Fe, Exp. 71 = .1006.

This experiment shows that no appreciable oxidation takes place in the final stage of the operation.

Experiments were next carried out by introducing varying amounts of KHF_2 with the NaF (F.G.B.), still adhering to the 10 : 1 mixture of flux and garnet. The KHF_2[10] was added to generate HF during the heating stage to displace the air and prevent oxidation from this source. A small vent was left at the top of tube to allow the HF to escape.

EXPERIMENTS WITH 10 : 1 MIXTURE OF NaF, KHF_2 : GARNET.

Exp.	Garnet 806.	NaF F.G.B.	KHF_2	Temp.	Time.	FeO.	FeO.	Conditions.
						gms.	%	
62	·3	2·7	·3	850—960°C.	15′	·0624	20·8	Sinter same as with NaF alone. Yellow solution.
64	·3	2·5	·5	960—1040°C.	5′	·0375	12·5	do.
65	·3	2·5	·5	do.	10′	·0429	14·3	Fusion; combination with glass. Yellow solution.
66	·3	2·0	1·0	do.	5′	·0279	9·3	do.

The introduction of the KHF_2 did not have the desired effect as the FeO figure obtained in all cases was low. The yellow colour of the solutions indicates that oxidation has occurred. The best conditions and highest results have been obtained with sodium fluoride alone.

The pure NaF (F.G.B.) used in the previous experiments has a pH value of 4.2 to Brom-cresol green. The KHF_2 used has a pH value of 2.4 to Thymol blue. There is therefore the possibility of some acid fluoride being present in the NaF. Three experiments were next carried out with NaF (F.G.B.) heated to 850-960° C. to drive off any HF and convert the $NaHF_2$ to NaF.

EXPERIMENTS WITH 10 : 1 MIXTURE NaF : GARNET.

Exp.	Garnet 806.	NaF (F.G.B.) 850—960°.	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
68	·3	3·0	960—1040°C.	10′	·0597	19·9	Sinter—partial fusion.
69	·3	3·0	850—960°C.	15′	·0639	21·3	do. do.
70	·3	3·0	do.	15′	·0639	21·3	do. do.

The sintering with NaF (F.G.B.) heated to 850-960° C. did not give any better results than when sintered with original NaF (F.G.B.).

Sodium Fluoride (F.G.B. pure).

Experiments were carried out on this material to test its purity.

Effervescence takes place with 5EHCl, and not with NaF prepared in the laboratory.

The pH value—4.2—is well on the acid side for neutral NaF.

Analysis	...	Na_2O	71·6 %
		Na	52·8 %
		F	44·20 %
NaF contains theoretically			
		Na	54·76 %
		F	45·24 %

These tests show that some $NaHF_2$ is present in this material.

Sodium fluoride neutral was prepared in the laboratory by neutralising NaOH (BDH., AR) with HF (Baker's Anal. C.P.) using litmus papers as indicators.

Experiments with 10 : 1 mixture NaF : garnet.

Exp.	Garnet 806.	NaF (Lab.).	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
72	·3	3·0	960—1040°C.	10′	·0846	28·2	Sinter—part fusion. Little combination with glass.

The results upon garnet No. 806 obtained from the foregoing show that only three experiments have given figures for FeO which are anyway near the figures obtained by the HF and H_2SO_4 methods—29.18 per cent. FeO. They are two preliminary experiments, 33 and 35, and the last experiment 72.

Exp. 33	...	29·56 % FeO
„ 35	...	28·30 % „
„ 72	...	28·20 % „

These three experiments were carried out upon sodium fluoride prepared in the laboratory from analytical reagents. The first two were prepared from Na_2CO_3 (BDH., AR.) and HF (Baker's Anal. C.P.) and the last from NaOH (BDH., AR) and HF (Baker's Anal. C.P.).

The experiments carried out with NaF (F.G.B.) alone gave figures ranging from 66.83 per cent. of the FeO obtained by HF and H_2SO_4 method. These figures show that a large proportion of the FeO can be determined and in the case of the neutral NaF prepared in the laboratory nearly the whole of it. It was therefore decided to prepare—

1. Pure neutral NaF from NaOH (BDH., AR) and HF (Baker's Anal. C.P.).
2. $NaHF_2$ from the above neutral NaF and HF (Baker's Anal. C.P.).
3. Pure neutral KF from KOH (BDH., AR) and HF (Baker's Anal. C.P.).
4. Pure CaF_2 from $CaCO_3$ (BDH., AR.) and HF (Baker's Anal. C.P.).

and to carry out experiments on these pure compounds, both alone and in mixtures, still adhering to the 10 : 1 flux mineral mixture.

PREPARATION OF PURE NEUTRAL SODIUM FLUORIDE.

A solution of NaOH (BDH., AR) was neutralised by careful addition of diluted HF (Baker's Anal. C.P.) until a pH value of 7.0 was obtained with Brom-thymol Blue: a spotting tile was used for this indicator. The solution containing separated NaF was evaporated to dryness on a water bath, finished off on a sand bath at a temperature of about 250° C.

The pH value of the solution had not altered on being heated to temperature of sand bath.

EXPERIMENTS WITH 10 : 1 MIXTURE NaF : GARNET.

Exp.	Garnet 806.	NaF Neutral 250°C.	Temp.	Time.	FeO. gms.	FeO. %	Conditions.
77	·3	3·0	850—960°C.	15′	·0639	21·3	Black sinter showing partial fusion and combination with glass.
86	·3	3·0	do.	15′	·0801	26·7	Black sinter; no combination with glass. Some mineral unattacked.

In Exp. 86 the NaF neutral was calcined at 600° C.

Consideration was given to the possibility of platinum being present, causing oxidation by catalysis upon heating.

Sodium fluoride neutral was prepared in silica ware only and comparative experiments run with sodium fluoride neutral prepared in platinum ware with the following results.

EXPERIMENTS WITH 10 : 1 MIXTURE NaF : GARNET.

Exp.	Garnet 806.	NaF Neutral 600°C.	Temp.	Time.	FeO. gms.	FeO. %	Conditions.
87	·3	3·0	850—960°C.	25′	·0828	27·6	NaF prepared in SiO_2 ware. All material carefully dried. Sinter similar to Exp. 86. Some mineral unattacked.
88	·3	3·0	850—960°C.	20′	·0849	28·3	NaF prepared in Pt. ware. Conditions as in Exp. 87.
91	·3	3·0	960—1040°C	15′	·0375	12·5	Fusion and combination with glass.

These results show that the use of platinum ware for the preparation of the sodium fluoride is not harmful.

In these experiments unattacked garnet was observed.

Experiments with a view to obtaining complete attack upon the garnet by either increasing the temperature or increasing the length of time of heat treatment were carried out, and all materials were dried before mixing and sealing.

Experiments with 10 : 1 mixture NaF : garnet.

Exp.	Garnet 806.	NaF 600°C.	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
93	·3	3·0	1040—1150°C.	15′	·0246	8·2	All material dried. Fusion and combination with glass. All mineral attacked. Some fusion undissolved.
98	·3	3·0	850—960°C.	45′	·0354	11·8	All material dried. Sinter. Some unattacked mineral.

Increase in temperature to 1040-1150° C. caused decomposition of the mineral but combination with glass, which being difficultly soluble, caused low results for FeO.

Longer heat treatment at temperature of 850-960° C. did not completely decompose the mineral.

It was decided to repeat Exps. 87 and 88 for verification and further information.

Repetition of Exps. 87 *and* 88.—Sintering with dried and undried sodium fluoride with garnet.

Experiments with 10 : 1 mixture NaF : garnet.

Exp.	Garnet 806.	NaF 600°C.	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
102	·3	3·0	850—960°C.	20′	·0828	27·6	NaF dried. Mineral not completely decomposed.
103	·3	3·0	do.	20′	·0828	27·6	NaF not dried. Mineral not completely decomposed.

These results verify the results obtained in Exps. 87 and 88 and prove *that sintering with neutral sodium fluoride at temperature of* 850-960° *C. does not completely decompose the garnet.* There does not appear to be any necessity to dry the mixture before sealing and heating.

As a result of the experiments carried out on sodium fluoride alone, it was decided to carry out experiments by introducing a lower M.P. substance into the mixture of sodium fluoride and garnet in an attempt to lower the M.P. of the mixture and so obtain fusions at the temperature of 850-960° C. without combination with the glass.

EXPERIMENTS WITH 10 : 1 MIXTURE OF NaF, NaOH : GARNET.

Exp.	Garnet 806.	NaF 600°C.	NaOH.	Temp.	Time.	FeO.	FeO.	Conditions.
						gms.	%	
83	·3	2·5	·5	850—960°C.	10′	·0564	18·8	Sinter. Some mineral unattacked.
85	·3	2·5	·5	do.	18′	·0549	18·3	do. do.
82	·3	1·5	1·5	do.	8′	·0270	9·0	Fusion and partial combination with glass.
84	·3	1·5	1·5	do.	5′	·0153	5·1	Semi-fusion reddish in colour showing oxidation of the FeO. Combined with glass.

The deliquescent nature of the NaOH made the mixing of the flux with the mineral a difficult operation. The presence of the water introduced with the NaOH must be considered as a possible source of oxidation of FeO.

J. Newton Friend in "The Text Book of Inorganic Chemistry," Vol. II., p. 148, gives two equations showing the liberation of chlorine on heating with SiO_2 in presence of H_2O and O up to 1000° C.

$$2x\text{NaCl} + y\text{SiO}_2 + x\text{H}_2\text{O} = x\text{Na}_2\text{O}.y\text{SiO}_2 + 2x\text{HCl}. \quad 4\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{Cl}_2$$

If this occurs there is the possibility of the liberation of fluorine under the similar conditions with a consequent oxidation of the FeF_2.

As a result of the above experiments the introduction of NaOH into the flux was discontinued.

Experiments with KF prepared in the laboratory alone and mixed with NaF (600° C.) were carried out for the reasons outlined under the experiments carried out with NaOH.

PREPARATION OF PURE NEUTRAL POTASSIUM FLUORIDE.

A solution of KOH (BDH., AR) was neutralised with HF (Baker's Anal. C.P.) to a pH value of 7.0 with Brom Thymol Blue in a similar manner to the preparation of the sodium fluoride. It was evaporated to dryness upon a water bath and calcined at a temperature of 600° C. After calcining, the KF was found to be of uneven composition, some pieces being quite alkaline and others reacting acid. Heat was evolved when the calcined KF was dissolved in water, the solution reacting alkaline. Dissociation had taken place according to the equation $2\text{KF} + \text{H}_2\text{O} \longrightarrow \text{K}_2\text{O} + 2\text{HF}$. Experiments taken of the pH value of the $KF.2H_2O$ formed by evaporating upon water bath and heating at various temperatures were carried out:—

100°C.	...	pH 6·8
130°C.	...	... 6·8
200°C.	...	... 6·8
600°C.	...	... 7·0

The 600° C. product when heated in the closed tube showed only a trace of water.

Experiments with 10 : 1 mixture of KF (600° C.) : garnet.

Exp.	Garnet 806.	KF 600°C.	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
90	·3	3·0	850—960°C.	10′	·0807	26·9	Partial fusion. Combination with glass. Fusion not completely soluble.

The KF, owing to its deliquescent nature, was dried on sand bath, mixed with garnet, and sealed quickly. Water was picked up before the operation could be completed.

Experiments with 10 : 1 mixture of NaF and KF : garnet.

Exp.	Garnet 806.	NaF 600°C.	KF 600°C.	Temp.	Time.	FeO	FeO.	Conditions.
						gms.	%	
92	·3	2·5	·5	850—960°C.	15′	·0744	24·8	Partial fusion. Yellow solution.
94	·3	2·5	·5	do.	15′	·0807	26·9	Mixture in tube dried at 100° for 1 hour. Partial fusion. Yellow solution.
96	·3	2·5	·5	do.	15′	·0549	18·3	do. do.
104	·3	2·5	·5	do.	15′	·0786	26·2	Mixture carefully dried at 130°C. Sinter partial fusion. Yellow solution.
105	·3	2·5	·5	do.	15′	·0783	26·1	No drying precautions. Sinter—partial fusion. Yellow solution.
106	·3	2·0	1·0	do.	15′	·0846	28·2	More fusion than in Exp. 92, 94, 104, 105. Similar to Exp. 108.
108	·3	2·0	1·0	800°C.	15′	·0870	29·0	Sinter—little fusion. Pale yellow solution. All mineral apparently attacked.
109	·3	2·0	1·0	850—960°C.	15′	·0822	27·4	More fusion than in Exp. 106 due to higher temp. Combination with glass. All mineral apparently attacked.
111	·3	2·0	1·0	under 800°C.	15′	·0870	29·0	Similar conditions to Exp. 108. All mineral attacked.

Exp's. 92-96. All tubes and reagents dried before filling and sealing.

These experiments did not give any higher results than those obtained with the NaF alone. The presence of KF lowered the M.P. of the mixture, giving partial fusions and more complete decomposition of the mineral. The yellow colour of the solutions indicates some oxidation of the FeO.

Exp's. 106, 108, 109, 111. with a mixture of 2.0 grms. NaF and 1.0 grm. KF gave consistently higher results than those obtained with NaF

alone. The increased amount of KF resulted in more complete fusions and, at temperatures of about 800° C., very little combination with glass took place, with apparent complete decomposition of the garnet. Further experiments were carried out to confirm these results.

EXPERIMENTS WITH 10 : 1 MIXTURE OF KF, NaF : GARNET.

Exp.	Garnet 806.	NaF 600°C.	KF 600°C.	Temp.	Time.	FeO.	FeO.	Conditions.
						gms.	%	
112	·3	2·0	1·0	800°C	15′	·0837	27·9	Similar conditions to Exp. 111. Mineral unattacked. Pale yellow solution.
113	·3	2·0	1·0	850°C	15′	·0786	26·2	More fusion than in Exp. 112. Yellow solution.
114	·3	2·0	1·0	700—800°C.	15′	·0786	26·2	Sinter. Very little fusion.

Whilst the high figures of Exps. 106, 108, 109, and 111 are not confirmed, improved conditions of the partial fusion, with very little combination with the glass at temperatures at 800° C. were obtained. There appears to be a little oxidation of the FeO when the colour of the solution is taken into consideration.

The deliquescent nature of the KF renders the materials hard to mix.

Further experiments were carried out in repetition of the above with the following results:—

EXPERIMENTS WITH 10 : 1 MIXTURE OF KF, NaF : GARNET.

Exp.	Garnet 806.	NaF 600°C.	KF 600°C.	Temp.	Time.	FeO.	FeO.	Conditions.
						gms.	%	
161	·3	2·0	1·0	800—850°C.	15′	·0765	25·5	Dried 2 hours, mixed and sealed while hot. Partial fusion. Yellow solution.
163	·3	2·0	1·0	800°C.	15′	·0660	22·0	Sinter-fusion, reddish at top due to oxidation. Yellow solution.
164	·3	2·0	1·0	700°C.	15′	·0432	14·4	Sinter. Some unattacked mineral.
165	·3	2·0	1·0	800°C.	15′	·0699	23·3	Sinter—fusion. Yellow solution.

These figures do not confirm the highest results obtained in Exps. 106, 108, 109, 111. The yellow solution denotes oxidation of the FeO.

The experiments carried out with mixtures of sodium fluoride, and the lower melting point potassium fluoride not proving satisfactory, experiments were next conducted by introducing the higher melting point calcium

fluoride into the sodium fluoride garnet mixture to see if the garnet could be decomposed without oxidation and combination with the glass by sintering.

Experiments were first carried out using NaF prepared in the laboratory and CaF_2 (pure Kahlbaum).

Experiments with 10 : 1 mixture NaF, CaF_2 : garnet.

Exp.	Garnet 806.	NaF 600°C.	CaF_2 Kahlbaum.	Temp.	Time.	FeO.	FeO.	Conditions.
						gms.	%	
121	·3	2·5	·5	960—1040°C.	15′	·0780	26·0	Partial fusion. Combination with glass. Incomplete solubility.
122	·3	2·5	·5	850—960°C.	15′	·0885	29·5	Hard black sinter. No combination with glass. Black scum on solution.
123	·3	2·5	·5	850—960°C.	15′	·0885	29·5	do. do.
124	·3	2·0	1·0	do.	15′	·0732	24·4	Hard black sinter. Disintegrates with difficulty.

Kahlbaum's CaF_2 on examination was found to contain paraffin, probably from the stopper; this accounted for the black scum noticed in Exp. 124.

Experiment 121 at the higher temperature of 960-1040° C. partly combined with the glass, whilst Exp. 124 with the increased amount of CaF_2 gave a hard sinter which did not completely disintegrate on boiling. An experiment was therefore carried out under conditions pertaining to Exp. 122, and 123 with CaF_2 prepared in the laboratory from $CaCO_3$ (BDH., A.R.) and HF (Baker's Anal. C.P.).

Experiments with 10 : 1 mixture NaF, CaF_2 : garnet.

Exp.	Garnet 806.	NaF 600°C.	CaF_2 Lab.	Temp.	Time.	FeO.	FeO.	Conditions.
						gms.	%	
125	·3	2·5	·5	850—960°C.	15′	·0807	26·9	Sinter similar to Exp. 121—123. No black scum.

This experiment, in the absence of organic material, gave a lower result than Exps. 122 and 123.

Experiments were carried out introducing sufficient carbon to reduce all the iron present calculated as Fe_2O_3 to FeO.

EXPERIMENTS WITH 10 : 1 MIXTURE OF NaF, CaF_2: GARNET WITH CARBON.

Exp.	Garnet 806.	NaF 600°C.	CaF_2 Lab.	C.	Temp.	Time.	FeO.	FeO.	Conditions.
							gms.	%	
126	·3	2·5	·5	·05	850—960°C.	15′	·0906	30·2	Sinter similar to Exps. 122, 123 and 125.
127	·3	2·5	·5	·007	do.	15′	·0894	29·8	do. do.

The FeO figure obtained in Exp. 126 calculated to Fe_2O_3 is 33.5 per cent. The total iron in the sample calculated to Fe_2O_3 is 35.6 per cent. This figure should be obtained if the mineral is completely decomposed.

To ascertain whether the whole of the garnet had been decomposed, further experiments were run under similar conditions to Exps. 126, 127, with a microscopic examination of any residue after solution of the fusion.

EXPERIMENTS WITH 10 : 1 MIXTURE OF NaF, CaF_2: GARNET WITH CARBON.

Exp.	Garnet 806.	NaF 600°C.	CaF_2 Lab.	C.	Temp.	Time.	FeO.	FeO.	Conditions.
							gms.	%	
157	·3	2·5	·5	·01	900°C.	15′	·0897	29·9	Hard stone-like sinter. No combination with glass. Undecomposed garnet.
158	·3	2·5	·5	·01	900°C.	20′	·0801	26·7	More vesicular than Exp. 157. Partial combination with glass.
152	·3	2·5	·5	·007	700—800°C.	60′	·0876	29·2	Similar to Exp. 157. Undecomposed garnet.
154	·3	2·5	·5	·007	800°C.	60′	·0825	27·5	do. do.
155	·3	2·5	·5	·007	850°C.	60′	·0828	27·6	More vesicular than Exp. 154. Undecomposed garnet.
156	·3	2·5	·5	·007	900°C.	60′	·0831	27·7	do. do.

A microscopic examination revealed the presence of undecomposed garnet grains. This confirmed the opinion formed as a result of the previous experiments—that the low FeO figure is due to this cause.

Discussion.

A review of the experiments using the 10 : 1 mixture of NaF : garnet at varying temperatures and times showed that—

1. The best conditions were obtained by sintering at temperatures of 850-960° C. for a period of 15 to 20 minutes, the FeO results varying from 21.3 to 28.32 per cent. These inconsistent results were due mainly to varying amounts of undecomposed mineral, noticed in most of these experiments.

2. Partial fusions were obtained by heating at temperatures of 960-1040° C. for 10 to 15 minutes, the FeO results varying from 12.54 to

29.6 per cent. These inconsistent results are due both to small amounts of undecomposed mineral and combination with the glass to a variable extent. The melting point of NaF is 980° C., which lies between the extreme ranges of temperature at which these experiments were conducted.

3. Complete fusions were obtained at temperatures between 1040° and 1150° C. by heating over a period of 15 minutes with excessive combination with the glass, giving the low result for FeO of 8.25 per cent. The mineral was completely attacked in this case.

As a result of these experiments with NaF alone it was concluded that whilst complete decomposition of the garnet can be obtained at temperatures above 980° C., the melting point of the NaF, the combination with the glass precluded the possibility of accurate results being obtained. Also by sintering at lower temperatures than 980° C. the garnet was not completely decomposed.

The results obtained by heating garnet with KF and mixtures of KF and NaF in the proportion of 10 parts of flux to one of mineral at varying temperatures showed that—

The best conditions were obtained by heating 10 : 1 mixtures of flux : garnet at a temperature of 800° C. for 15 minutes when the proportion of NaF.KF was 2 : 1 and 850-960° C. when the proportion was 5 : 1. The former gave results varying from 14.4 to 29.0 per cent. FeO and 18.3 to 26.2 per cent. FeO in the latter. Under these conditions complete decomposition of the garnet was obtained with very little combination with the glass. The temperature required controlling carefully as an appreciable rise caused increased combination with the glass.

Why these low and inconsistent results should be obtained is not definitely known, but it is possible that they may be caused by the introduction of water from the hygroscopic KF whilst mixing. See page 183 re behaviour of KF on calcining at 600° C. and equations showing reaction on heating NaCl, SiO_2 and water.

The results obtained with 6 : 1 mixture of KHF_2 : garnet were altogether unsatisfactory as the liberation of HF caused the tubes to blow out, and the low melting point of the KHF_2 caused excessive combination with the glass. The FeO results varied from nil to 7.7 per cent.

With mixtures of NaF and KHF_2 in the proportion of 9 : 1 and the flux : garnet ratio of 10 : 1 results varying from 9.3 to 20.8 per cent. FeO were obtained by heating at temperatures of 850°-1040° C. In all cases the yellow solution indicated oxidation of FeO.

When CaF_2 was introduced into the NaF : garnet mixture, the best conditions were obtained by heating 10 : 1 mixtures of flux : garnet at temperatures of 850°-960° C. for 15 minutes when the proportion of CaF_2 : NaF was 1 : 5. Experiment 125, the only one without carbon, gave a figure of 26.9 per cent. FeO. Experiments 152, 154-8 showed that under these conditions garnet was incompletely decomposed. An increase in temperature to 960°-1040° C. caused combination with the glass, and the increased ratio of CaF_2 : NaF of 1 : 2 at temperatures of 850°-960° C., gave a sinter which did not disintegrate completely.

EXPERIMENTS WITH SODIUM PYROBORATE.

The effect of sodium pyroborate upon the decomposition of the garnet was next tried as it was considered there would be very little action upon the glass on account of its low melting point and acidity as a flux.

Melting point 561° C., 734° C., 741° C., 878° C.

GARNET SAMPLE.

The sample of garnet, Lab. No. 806, being exhausted, a further sample, Lab. No. 735/32 from the same district, Yabberup, was prepared, analysed, and used in the subsequent investigations.

Analysis, 735/32.

	%
SiO_2 ...	... 35·29
Al_2O_3 ...	... 19·25
Fe_2O_3 ...	... 3·31
*FeO ...	... 30·30
MnO ...	... 1·47
CaO ...	... 3·50
MgO ...	... 3·36
H_2O+ ...	... ·62
H_2O- ...	... *Nil*
TiO_2 ...	... 3·14
Total	100·24

*By HF and H_2SO_4 method.

EXPERIMENT WITH 5 : 1 MIXTURE OF $Na_2B_4O_7$: GARNET.

Exp.	Garnet 735/32.	$Na_2B_4O_7$	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
171	·3	1·5	850—960°C.	15′	·0732	24·4	Dark bottle green fusion. No combination with glass. Undecomposed garnet.
172	·3	1·5	do.	30′	·0765	25·5	Dark bottle green fusion. No combination with glass. Undecomposed garnet. Yellow solution.
173	·3	1·5	do.	30′	·0789	26·3	do. do.
174	·3	1·5	do.	45′	·0801	26·7	do. do.
175	·3	1·5	do.	60′	·0768	25·6	do. do.

These experiments showed that fusions with $Na_2B_4O_7$ whilst not exhibiting any appreciable attack upon the glass, dissolved in H_2SO_4 to a yellow solution, leaving a residue of undecomposed garnet.

Experiments mixing NaF with $Na_2B_4O_7$ were next carried out in an attempt to completely decompose the garnet without excessive combination with the glass.

It was found impossible to mix the fluxes without the introduction of water into the tubes owing to the rate at which anhydrous boric acid picks it up. Further experiments were all rejected owing to the difficulty in controlling the fusions.

The effect of fusing together NaF and B_2O_3 before mixing with the garnet was next tried and an investigation of the constitution of this product undertaken.

NOTES ON THE PROPERTIES OF FLUOBORIC ACID AND FLUOBORATES.

Berzelius[14] says that HF and Boric acid together give $H_2B_2O_4.6HF$. This is thought to be a mixture of metaboric acid, hydrofluoboric acid, and HF.

Abegg, Fox and Henry[15] tried reactions between Boric acid, HF and KF with no definite conclusion.

Friend[15] says, "Although no fluoboric acids are definitely known, two compounds have been formed which may be looked upon as salts of such acids." They are:—

$B_2O_3.(KF)_3$

$(B_2O_3).(KF)_2.K_2O$

The first of these is formed by fusing together two molecular proportions of KF with one of B_2O_3 and allowing the melt to cool slowly.

The second by fusing the former with the requisite amount of K_2CO_3.

These compounds dissolve, without decomposition, in a little water, but with much water they decompose.

Mellor[16] says, "Most of our knowledge of the fluoborates is still in the state left by Berzelius."

Preparation of Sodium Fluoborates.

To decide the proportions of B_2O_3 and NaF to be fused together to form sodium fluoborates, consideration was first given to the known Boric acids and Borates and the possible fluoborates formed from them by substituting 2NaF for Na_2O.

The known Boric acids[17] are:—

1. Orthoboric acid $(H_2O)_3.B_2O_3$.
2. Metaboric acid $H_2O.B_2O_3$.
3. Pyro or tetraboric acid $H_2O.(B_2O_3)_2$. This acid is assumed by chemists. Its Sodium salt, Borax, is well known.

The sodium salts[18] of these acids are:—

1. Sodium orthoborate $(Na_2O)_3.B_2O_3$. There are very few orthoborates known.
2. Sodium metaborate $Na_2O.B_2O_3$.
3. Sodium pyro or tetraborate $Na_2O.(B_2O_3)_2$.

The possible fluoborates analogous with these borates are:—

1. Sodium orthofluoborate $(NaF)_6.B_2O_3$.
2. Sodium metafluoborate $(NaF)_2B_2O_3$. The potassium salt of this constitution is referred to by Friend and recorded above.
3. Sodium pyrofluoborate $NaF.B_2O_3$.

As the sodium metaborate has been prepared and the potassium salt of metafluoboric acid has been referred to, it was decided to attempt to prepare sodium metafluoborate by fusing together 2 molecular proportions of NaF and 1 of B_2O_3 in a platinum dish at temperatures of about 1000° C. (this is above the M.P. of NaF) and to carry out experiments with this product. This fused product was ground and sieved so that it could be mixed with the garnet.

Experiments with 5 : 1 mixture Sodium Metafluoborate : garnet.

Exp.	Garnet 735/32.	$(NaF)_2$ B_2O_3	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
187	·5	2·5	600—700°C.	30′	·1485	29·7	Silver grey vesicular sinter. No bubbling or swelling. Dark coloured flocculent residue.
189	·5	2·5	600—700°C.	30′	·1465	29·3	do. do
191	·3	1·5	700—800°C.	30′	·0918	30·6	do. do.
192	·4	2·0	do.	30′	·1188	29·7	do. do.
195	·4	2·0	do.	30′	·1204	30·1	do. do.
206	·4	2·0	do.	30′	·1204	30·1	do. do.

The dark coloured flocculent residue noticed in these experiments indicated the presence of carbonaceous material which would give high and erroneous results for FeO.

The following reagents were tested for carbon by dissolving in water and fuming with sulphuric acid:—

Boric acid (B.D.H., B.P.), Carbon present.
„ „ (B.D.H., A.R.), Carbon absent.
Sodium fluoride (Lab.), Carbon absent.

Carbon free sodium fluoborate was prepared by fusing together two molecular parts of NaF (prepared in the laboratory and calcined at 600° C.) and one part of anhydrous B_2O_3 glass (prepared from Boric acid (B.D.H., A.R.) in an electric furnace at temperature of about 1000° C. This fused product was ground in diamond and agate mortars without sieving.

Experiments with 5 : 1 mixture sodium metafluoborate (carbon free) : garnet.

Exp.	Garnet 735/32.	$(NaF)_2$ B_2O_3	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
206	·4	2·0	700—800°C.	30′	·1188	29·7	Silver grey vesicular partial fusion. No dark-coloured residue.
207	·4	2·0	700—800°C.	30′	·1280	32·0	More fusion than Exp. 206. Small amount of carbonaceous material. Discard.
208	·4	2·0	700—800°C.	30′	·1204	30·1	Less fusion than Exp. 207. No carbonaceous material.
209	·4	2·0	700—800°C.	30′	·1284	32·1	Similar to 208.

The FeO figures in Experiments 206 and 208 are close to the figure obtained by the HF and H_2SO_4 method, 30.3 per cent. FeO. Experiments 207 and 209 gave higher results, the latter being free from carbonaceous material.

A further series of experiments were carried out with carbon free sodium metafluoborate and garnet crushed to pass –90 mesh only with no further fine grinding.

EXPERIMENTS WITH 5 : 1 MIXTURE SODIUM METAFLUOBORATE (CARBON FREE) : GARNET—90 MESH.

Exp.	Garnet 735/32. —90 mesh.	$(NaF)_2$ B_2O_3	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
210	·5	2·5	700—800°C.	30′	·1565	31·3	Similar to Exp. 209.
211	·5	2·5	do.	30′	·1565	31·3	do. do.
212	·5	2·5	—700°C.	30′	...	...	Incomplete decomposition of garnet.
213	·5	2·5	700—800°C.	30′	·1505	30·1	Partial fusion. Incomplete decomposition of garnet.

Experiments 206-213 carried out with carbon free sodium metafluoborate gave FeO figures varying from 29.7 per cent. to 32.1 per cent. Experiment 213 with –90 mesh garnet at temperatures of 700-800° C. showed undecomposed garnet grains in the residue and an FeO figure of 30.1 per cent. These figures are higher and more consistent than the figures obtained with the fluxes previously tried.

Experiments 214-225 were carried out at increased temperatures of 800 to 960° C. for varying times with -90 mesh garnet in an attempt to obtain complete decomposition of garnet.

EXPERIMENT WITH 5 : 1 MIXTURE $(NaF)_2.B_2O_3$: GARNET.

Exp.	Garnet 735/32.	$(NaF)_2$ B_2O_3	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
214	·4	2·0	800—850°C.	20′	·1276	31·91	Silver grey vesicular fusion. No carbonaceous material. Fusion completely soluble.
218	·4	2·0	800—900°C.	20′	·1259	31·47	Similar to Exp. 214.

The best conditions were observed in Experiments 214 and 218, and the FeO figures were higher than those obtained by the HF and H_2SO_4 method, 30.30 per cent. Experiment 219 was carried out to see if $(NaF)_2.B_2O_3$ had any action upon $KMnO_4$.

CONTROL EXPERIMENT.

Exp. 219.—1.5 grm. $(NaF)_2.B_2O_3$ was added to the dilute sulphuric acid solution, boiled, cooled under sodium bicarbonate seal as in the method and titrated with standard $KMnO_4$ solution. One drop of $KMnO_4$ solution gave faint pink colour, therefore no action has taken place causing the higher results.

Experiment with 5 : 1 mixture $(NaF)_2.B_2O_3$: garnet.

Exp.	Garnet 735/32. —90 mesh.	$(NaF)_2$ B_2O_3	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
220	·5	2·5	850—960°C.	25′	·1559	31·19	Silver grey compact fusion. Complete solution.
	Fine						
221	·4	2·0	do.	20′	·1241	31·03	do. do.
222	·4	2·0	do.	20′	·1248	31·21	Silver grey compact fusion. Complete solution. Slight combination with glass.
223	·5	2·5	900°C.	20′	·1580	31·60	Vesicular fusion. Complete solution.
	—90						
224	·4	2·0	900—960°C.	20′	·1262	31·56	Silver grey fusion. Complete solution.
225	·4	2·0	do.	20′	·1276	31·91	Similar to Exp. 224.

Experiments 220, 224-5 on –90 mesh garnet at temperatures between 850-960° C. gave FeO figures varying from 31.19-31.91 per cent. Experiments 221-223 on the finely ground garnet at similar temperatures gave FeO figures varying from 31.03-31.60 per cent. There is no necessity therefore to fine grind the garnet.

The best conditions were observed in Experiments 224-225 by fusing for 20 minutes at temperatures of 900-960° C. and confirm the previous best conditions observed in Experiments 214 and 218.

The FeO figure by the HF and H_2SO_4 method is 30.30 per cent. and a microscopic examination of the residue revealed grains of undecomposed garnet. The total iron figure calculated to FeO gives 33.48 per cent. FeO. The best figures obtained by fusion with $(NaF)_2.B_2O_3$ lie between these. Therefore the results obtained in series 220-225 must be considered satisfactory as they are the highest and most consistent figures yet obtained and justify further investigation.

The mean FeO value obtained by the fluoborate method at temperatures over 900° C. (Exp's. 223-5) is 31.69 per cent. FeO. This figure is verified when it is applied to the constitution of the garnet described in Part I. of the Paper.

CONSTITUTION OF THE FLUOBORATES.

At this stage it was decided to analyse the sodium metafluoborate used in Experiments 224-5 and to prepare and analyse for further experiments:

1. *Sodium metafluoborate* $(NaF)_2.B_2O_3$, Batch 239—by heating 6.03 gms. NaF (Lab) with 5.00 gms. B_2O_3 (prepared from Boric acid BDH., AR.) at 1000° C. until completely miscible.

2. *Sodium pyrofluoborate* $NaF.B_2O_3$, *Batch* 240—by heating 3.01 gms. NaF (Lab.) with 5.00 gms. B_2O_3 (BDH., AR.) at 1000° C. until completely miscible.

ANALYSIS OF $(NaF)_2.B_2O_3$ USED IN EXPERIMENTS 224-225.

	Anal.	Theoretical.
	%	%
F	16·17	24·73
Na	31·38	29·94
B_2O_3	...	45·33

ANALYSIS $(NaF)_2.B_2O_3$, BATCH 239.

	Anal.	Theoretical.
	%	%
F	18·75	24·73
Na	31·05	29·94
B_2O_3	45·62	45·33
	95·42	100·00

By Calculation.

	Anal.		NaF.		Na_2O.	B_2O_3	Total.
	%		%		%	%	%
F	18·75		18·75		...	...	18·75
Na	31·05		22·70		...	...	22·70
Na_2O		41·85		30·60	11·25	...	11·25
B_2O_3	45·62		...		...	45·62	45·62
Total ...	95·42		41·45		11·25	45·62	98·32

		$(NaF)_2.B_2O_3$	$Na_2O.B_2O_3$	Total.
	%	%	%	%
NaF	41·45	41·45	...	41·45
Na_2O	11·25	...	11·25	11·25
B_2O_3	45·62	34·36	12·64	47·00
Total ...	98·32	75·81	23·89	99·70

Possible Composition.

Sodium metafluoborate $(NaF)_2.B_2O_3$	75·81
,, metaborate $Na_2O.B_2O_3$	23·89
Total	99·70

The higher figure for B_2O_3, 47.00 per cent., obtained by calculation and the corresponding high total of 99.70 per cent. indicates a loss of B_2O_3 in the determination. c.f. Analysis of sodium pyrofluoborate, Batch 240.

ANALYSIS OF $NaF.B_2O_3$, BATCH 240.

	Anal. %	Theoretical. %
F	8·95	17·02
Na	21·61	20·60
B_2O_3	65·20	62·38
	95·76	100·00

By Calculation.

	Anal. %		NaF. %		Na_2O. %	B_2O_3 %	Total. %
F	8·95		8·95		...	...	8·95
Na	21·61		10·83		...	...	10·83
Na_2O		29·13		14·60	14·53	...	14·53
B_2O_3	65·20		...		...	65·20	65·20
Total ...	95·76		19·78		14·53	65·20	99·51

	%	$NaF.B_2O_3$ %	$Na_2O\ (B_2O_3)_2$ %	Total. %
NaF	19·78	19·78	...	19·78
Na_2O	14·53	...	14·53	14·53
B_2O_3	65·20	32·80	32·64	65·44
Total ...	99·51	52·58	47·17	99·75

Possible Composition.

Sodium pyrofluoborate $NaF.B_2O_3$	52·58
,, pyroborate $Na_2O\ (B_2O_3)_2$	47·17
Total	99·75

The B_2O_3 figure obtained by calculation, 65.44 per cent., checks closely the determined figure 65.20 per cent. c.f. Analysis of sodium metafluoborate, batch 239.

The analysis of the above products indicates a loss of fluorine during their preparation. In an attempt to overcome this loss further batches of sodium metafluoborate $(NaF)_2.B_2O_3$, were prepared under varying conditions and the fluorine determined.

PREPARATION OF $(NaF)_2.B_2O_3$, BATCH 255.

9.05 gms. of NaF (prepared in the laboratory) was placed in a Pt. dish with 7.50 gms. of coarsely broken fused B_2O_3 glass (prepared from Boric acid, BDH., AR) and heated in the electric furnace at 960° C. for the shortest possible time until miscible. This took 5 minutes. The fused product was cooled by pouring into a cold Pt. dish and finely ground.

F per cent.—22.3.

Under these conditions, when the time of heating is limited, the amount of fluorine is increased to within 2.43 per cent. of the theoretical.

PREPARATION OF $(NaF)_2.B_2O_3$, BATCH 277.

12.06 gms. NaF (Lab.) was placed in a Pt. dish with 10 gms. of coarsely broken fused B_2O_3 (same reagents as used in batch 255) and heated in the electric furnace at temperatures between 850-960° C. for 20 minutes stirring occasionally. No fumes were noticed on heating. The melt was poured into a cold Pt. dish as before. The product, a white, hard enamel-like substance, was finely ground.

F per cent.—23.19.

Under these conditions the figure for fluorine is 1.54 per cent. lower than the theoretical.

PREPARATION OF $(NaF)_2.B_2O_3$, BATCH 278.

This product was prepared in a similar manner to batch 277 except that the temperature was raised to 960-1040° C. and heated for 5 minutes only until miscible. Fumes were given off. The product was a white, enamel-like substance similar to batch 277.

F per cent.—23.52.

The fluorine figure here is increased to within 1.21 per cent. of the theoretical.

PREPARATION OF $(NaF)_2.B_2O_3$, BATCH 279.

This product was prepared in a similar manner to batch 277 except that the temperature was lowered to 750-850° C. and the mass constantly stirred at this temperature for 30 minutes. No fumes were noticed. The heated mass was pasty and not completely fused. On cooling it did not have the enamel-like appearance of batches 277 and 278.

F per cent.—22.91.

This figure is 1.82 per cent. lower than the theoretical.

In the preparation of these fluoborates the operations preparatory to heating were carried out in the shortest possible time to prevent the introduction of water per medium of the fused boric oxide glass.

The percentages of fluorine obtained were as follows:—

Batch No.	224–5	239	255	277	278	279
F %	16·17	18·75	22·30	23·19	23·52	22·91

These figures show that on limiting the time under the conditions of preparation in batches 277-9 the percentage of fluorine was increased considerably, the maximum figure obtained being 23.52 per cent. on heating 5 minutes. It is generally considered that in the determination of fluorine only about 95 per cent. is recovered, therefore it can be assumed that under the conditions of preparation of batches 277-9 nearly the whole of the fluorine is retained.

The analyses and calculations of batches 239 and 240 suggest that some of the fluorine is replaced by oxygen leaving a mixture of sodium metafluoborate and sodium metaborate in batch 239 and sodium pyrofluoborate and sodium pyroborate in batch 240.

EXPERIMENTS ON FERROUS IRON DETERMINATION WITH THE ABOVE SODIUM METAFLUOBORATES.

EXPERIMENT WITH $(NaF)_2.B_2O_3$, BATCH 239.

Exp.	Garnet 735/33.	$(NaF)_2$ B_2O_3	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
244	·3	1·5	900—960°C.	20′	·0956	31·87	Similar to Exps. 224–5.

EXPERIMENT WITH $NaF.B_2O_3$, BATCH 240.

Exp.	Garnet 735/33.	NaF B_2O_3	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
243	·3	1·5	900—960°C.	20′	·0923	30·76	Dark green fusion. Similar to borax fusion. Faint yellow solution.

EXPERIMENT WITH $(NaF)_2.B_2O_3$, BATCH 279.

Exp.	Garnet 735/33.	$(NaF)_2$ B_2O_3	Temp.	Time.	FeO.	FeO.	Conditions.
					gms.	%	
289	·4	2·0	900—960°C.	15′	·1264	31·60	Similar to Exps. 224–5.
291	·45	2·25	do.	15′	·1417	31·49	do. do.

The mean figure for Experiments 244, 289 and 291 with sodium metafluoborate is 31.65 per cent. FeO. This checks the previous mean figure of 31.69 per cent. FeO.

SUMMARY.

A survey of the methods in the literature at the disposal of the author is presented with the reasons necessitating the development of a new method. The hydrofluoric and sulphuric acid methods are not satisfactory with certain minerals, *e.g.*, tourmaline, on account of their refractoriness to these acids.

The complete experimental work carried out is described and consists of the investigation into the effect upon the decomposition of almandine garnet of various fluxes by fusing and sintering. The fluxes used were:— KOH, NaOH, KF, NaF, KHF_2, CaF_2 $Na_2B_4O_7$, $(NaF)_2.B_2O_3$, $NaF.B_2O_3$. Satisfactory results were obtained with sodium metafluoborate $(NaF)_2.B_2O_3$.

A consideration of the preparation, analysis and constitution of the fluoborates is presented with the determination of the ferrous iron values of almandine garnet by fusion with these substances.

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